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Original scientific paper

## Speciation of selected trace and major elements in lignite Used in "Nikola Tesla A" power plant (Obrenovac, Serbia)

ALEKSANDAR POPOVIĆ<sup>1\*#</sup> and DRAGANA DJORDJEVIĆ<sup>2</sup>

<sup>1</sup> Department of Chemistry, University of Belgrade, P. O. Box 158, 11001 Belgrade and

<sup>2</sup> ICTM - Chemistry Center, Njegoševa 12, 11000 Belgrade, Serbia and Montenegro.

**Abstract:** Four samples of milled lignite used in the "Nikola Tesla A" power plant, located in Obrenovac near Belgrade, were subjected to a five-step sequential extraction, comprising of the following phases: distilled water, 1 M ammonium acetate, 0.2 M ammonium oxalate/0.2 M oxalic acid, acidic solution of H<sub>2</sub>O<sub>2</sub> and a 6 M solution of HCl. The concentrations of the different elements obtained in the extractions were statistically analysed. The majority of the examined elements were found to be most probably associated with inorganic fractions of lignite, only aluminum, silicon, chromium and arsenic have a larger extractable organic/sulfide fraction than an extractable inorganic fraction. Aluminosilicates of magnesium (carriers of arsenic, zinc, lead, copper and chromium), silicates of potassium (scavengers of lead and nickel), mixed aluminates of iron and magnesium (carriers of arsenic, zinc, copper and chromium) and compounds of iron that do not contain aluminum and magnesium (scavengers of manganese) were dissolved in the fifth phase of the sequential extraction. Copper is a substrate of aluminosilicates of potassium and magnesium, while zinc and chromium are substrates of compounds of iron leached in the third phase of the sequential extraction. Interphase correlation revealed that the adsorbed and ion-exchangeable fractions of most of the examined elements do not exhibit preferential binding to the components of the inorganic matrix of lignite ash.

**Keywords:** lignite, trace elements, major elements, sequential extraction.

### INTRODUCTION

The chemical and physical characteristics of a coal are predetermined by the nature of the precursor plants, the amount of inorganic materials, and by the nature, intensity and duration of the biochemical and geochemical processes which were responsible for its formation.<sup>1</sup> The inorganic component of coal consists of discrete mineral fragments containing variously associated trace elements. Almost all natural elements have been found in coal,<sup>2</sup> except some very rare elements such as polonium, astatine, francium and protactinium.<sup>3</sup> In US coals, 79 elements have been found, starting from carbon (63 % average content). The most abundant heavy metal is lead (11 ppm aver-

\* Author for correspondence.

# Serbian Chemical Society active member.

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age), while ruthenium and osmium have been detected only at trace levels (1 ppb).<sup>3</sup> In coals from different parts of the world some precious elements have also been found, such as platinum,<sup>4</sup> but also radioactive elements, such as radium-226 and actinium-228.<sup>5</sup> In coals leaving less than 5 percent ash, trace elements mostly originate from organic components (*e.g.*, biogenic V and Ni), whereas in coals leaving more ash, they also originate from inorganic, mineral components.

During coal combustion in thermo-electric power plants, practically only the organic portion of coal burns, while the inorganic components of the coal mainly do not burn, but remain in the ash, which is a by-product of combustion. Since coal, by definition, contains more than 50 % of organic substances,<sup>6</sup> which are not found (or are found in the very small amounts) in the ash, it is clear that the main part of the inorganic components of coal, including many trace elements, is concentrated in the ash. A series of physico-chemical transformations takes place during coal combustion in power plants, often changing the solubility and association patterns of various elemental species. Moreover, the elements show various distribution patterns among the mineral fractions obtained after coal combustion, which are often completely different, to the original associations. It has been established that with the decrease of ash particle size the concentrations of arsenic, copper, molybdenum, lead and zinc increase. While quartz is carried through to the fly ash, pyrite and carbonates make a greater contribution to the bottom ash.<sup>7</sup> In coal ash obtained by the combustion of Nigerian coal, most of the elements examined had enrichment factors less than 1, while arsenic, iron, hafnium, sodium and titanium had enrichment factors ranging from 1 to 10.<sup>8</sup> Also, some of the elements, such as mercury, bromine and selenium, predominantly evaporate. The ash, produced by coal combustion, is stored in landfills where it is exposed to different influences.<sup>9,10</sup> These influences can solubilize some, otherwise sparingly soluble metals,<sup>11–13</sup> which can then contaminate the soil and surface and ground waters in the vicinity of the landfill.<sup>14,15</sup> Thus, environmental aspects of ash storage are increasing the already existing interest for trace and major elements in coal used in power plants.

In order to establish the distribution and major associations of selected trace and major elements in samples of milled lignite used in the "Nikola Tesla A" power plant located in Obrenovac near Belgrade, sequential extraction of lignite samples and statistical analysis of the extracted concentrations were performed. Establishment of mentioned distribution and associations in lignite may be important in predicting the chemodynamics of elements during lignite combustion and later, during exposure of the ash to the influence of the environment.

"Nikola Tesla A" power plant, together with its "twin", "Nikola Tesla B" power plant, uses lignite from the Kolubara Basin. The maximum daily consumption of lignite is approx.  $9 \times 10^7$  kg, and under these conditions, the amount of obtained ash is approx.  $1.7 \times 10^7$  kg per day.<sup>16</sup>

Sequential extraction is a powerful tool for predicting the behavior of trace elements under various environmental conditions (changes of pH, redox-potential

*etc.*). The use of sequential extraction for the analysis of coals and coal combustion by-products only started relatively recently,<sup>17</sup> but is now being widely used on samples from all over the world,<sup>18–21</sup> including samples of coal, fly and dump ash from Serbia.<sup>22–24</sup>

#### EXPERIMENTAL

During September 1997, November 1997, January 1998 and March 1998, ten samples per month of milled, prepared for combustion, lignite, were taken. The combined probes of 50 g, one per sampling month, were subjected to a five-step sequential extraction procedure. The procedure itself comprised the following sequence of extractants:

1. Distilled water (weakest extractant – the amount of elements extracted in this step is the least that can be expected, regardless of the type of water used for ash transport to the dump);
2. 1 M Ammonium acetate (this extractant should dissolve the fractions of elements that are bound to the particle surface with stronger bonds than the fraction washed with distilled water);
3. 0.2 M Ammonium oxalate/0.2 M oxalic acid (imitation of the reductive dissolution of iron and manganese oxides, which are important scavengers of microelements);
4. 30 % H<sub>2</sub>O<sub>2</sub>, 0.01 M HNO<sub>3</sub> on a water bath at 85 °C, in order to dissolve organic/sulfide matter, with subsequent desorption of eventually re-adsorbed elements, by washing with a 3.2 M ammonium acetate solution for 30 min. In the case of coals it can be expected that a large, but not all, portion of the organic and sulfide phases will be dissolved in this reagent. Consequently, a portion of the trace and major elements accompanying the undissolved organic/sulfide matrix will remain in the solid phase.
5. Digestion with 6 M HCl at 85 °C, introduced in order to obtain additional information on the crystalline iron oxides and silicates.

The elected sequence of extractants was, with some alterations,<sup>25</sup> mostly used for examination of coal samples,<sup>18–20</sup> and it is remarkably similar to the sequence of extractants used for sediments and soils.

After washing, the residues were treated with the next extractant. The combined extracts and washings after each extraction step were concentrated and the trace elements were analyzed by a SpectrAA-20+ Varian atomic absorption spectrometer.

#### RESULTS

The concentrations of the examined major and trace elements are shown in Tables I–III, while correlational parameters, obtained by statistical analysis of the extracted concentrations, are shown in Tables IV–VII.

#### DISCUSSION

The macro- and microelements contained in lignite were differently distributed (Tables I–III). However, it is obvious from the results obtained by extraction that most elements were contained in the inorganic phase of lignite, even inside the extractable part. It should not be forgotten that during sequential extraction the solid phase was not totally destroyed. A large amount, but not all, of the organic/sulfide component was dissolved in the fourth phase of sequential extraction, while the total mineral component was not dissolved either, which means that some elements have additional organic and mineral components, besides the ones determined by the extraction.

TABLE I. Concentrations of extracted major elements (ppm) from milled lignite samples used in the "Nikola Tesla" power plants

| Mg           | Phase I |       | Phase II |       | Phase III |       | Phase IV |       | Phase V |       | Total |
|--------------|---------|-------|----------|-------|-----------|-------|----------|-------|---------|-------|-------|
|              | ppm     | %     | ppm      | %     | ppm       | %     | ppm      | %     | ppm     | %     |       |
| Sample1      | 140.9   | 15.21 | 319.3    | 34.47 | 45.40     | 4.90  | 281.3    | 30.37 | 139.4   | 15.05 | 926.3 |
| Sample2      | 160.0   | 16.47 | 326.0    | 33.56 | 46.05     | 4.74  | 244.5    | 25.17 | 194.8   | 20.05 | 971.4 |
| Sample3      | 226.0   | 26.30 | 318.7    | 37.08 | 42.63     | 4.96  | 115.7    | 13.46 | 156.4   | 18.20 | 859.4 |
| Sample4      | 127.6   | 19.94 | 319.9    | 50.00 | 40.63     | 6.35  | 94.7     | 14.80 | 56.95   | 8.90  | 639.8 |
| Average      | 163.6   | 19.27 | 321.0    | 37.80 | 43.68     | 5.14  | 184.0    | 21.67 | 136.9   | 16.12 | 849.2 |
| St.deviation | 43.7    | 5.14  | 3.4      | 0.40  | 2.52      | 0.30  | 92.7     | 10.91 | 58.1    | 6.84  | 200.4 |
| Al           | Phase I |       | Phase II |       | Phase III |       | Phase IV |       | Phase V |       | Total |
|              | ppm     | %     | ppm      | %     | ppm       | %     | ppm      | %     | ppm     | %     |       |
| Sample1      | 17.49   | 1.03  | 0.00     | 0.00  | 439.8     | 25.85 | 1029     | 60.48 | 215.1   | 12.64 | 1701  |
| Sample2      | 36.47   | 1.96  | 0.00     | 0.00  | 452.5     | 24.31 | 1104     | 59.32 | 268.2   | 14.41 | 1861  |
| Sample3      | 44.57   | 2.53  | 0.20     | 0.01  | 426.7     | 24.19 | 1052     | 59.65 | 240.2   | 13.62 | 1764  |
| Sample4      | 99.42   | 7.68  | 0.00     | 0.00  | 408.7     | 31.56 | 692.5    | 53.47 | 94.42   | 7.29  | 1295  |
| Average      | 49.49   | 2.99  | 0.05     | 0.00  | 431.9     | 26.09 | 969.4    | 58.56 | 204.5   | 12.35 | 1655  |
| St.deviation | 35.17   | 2.12  | 0.10     | 0.01  | 18.7      | 1.13  | 187.2    | 11.31 | 76.5    | 4.62  | 318   |
| Si           | Phase I |       | Phase II |       | Phase III |       | Phase IV |       | Phase V |       | Total |
|              | ppm     | %     | ppm      | %     | ppm       | %     | ppm      | %     | ppm     | %     |       |
| Sample1      | 194.5   | 4.39  | 127.2    | 2.87  | 243.7     | 5.51  | 2792     | 63.08 | 1069    | 24.15 | 4426  |
| Sample2      | 253.0   | 4.80  | 150.9    | 2.86  | 263.2     | 5.00  | 3010     | 57.15 | 1590    | 30.19 | 5267  |
| Sample3      | 221.5   | 4.99  | 116.1    | 2.61  | 221.1     | 4.98  | 2375     | 53.48 | 1507    | 33.94 | 4441  |
| Sample4      | 349.9   | 11.35 | 102.6    | 3.33  | 190.3     | 6.17  | 1871     | 60.68 | 569.5   | 18.47 | 3083  |
| Average      | 254.7   | 5.92  | 124.2    | 2.89  | 229.6     | 5.33  | 2512     | 58.36 | 1184    | 27.50 | 4304  |
| St.deviation | 67.8    | 1.58  | 20.4     | 0.47  | 31.3      | 0.73  | 502      | 11.66 | 469     | 10.90 | 1091  |

TABLE I. Continued

| K            | Phase I |       | Phase II |       | Phase III |       | Phase IV |       | Phase V |       | Total |
|--------------|---------|-------|----------|-------|-----------|-------|----------|-------|---------|-------|-------|
|              | ppm     | %     | ppm      | %     | ppm       | %     | ppm      | %     | ppm     | %     |       |
| Sample1      | 29.39   | 17.63 | 37.58    | 22.54 | 17.29     | 10.37 | 72.57    | 43.52 | 9.92    | 5.95  | 166.8 |
| Sample2      | 32.09   | 18.52 | 55.73    | 32.17 | 18.79     | 10.85 | 52.74    | 30.44 | 13.89   | 8.02  | 173.2 |
| Sample3      | 32.78   | 15.99 | 103.9    | 50.70 | 16.39     | 8.00  | 37.78    | 18.43 | 14.09   | 6.88  | 204.9 |
| Sample4      | 38.27   | 32.60 | 39.97    | 34.05 | 12.79     | 10.89 | 17.99    | 15.32 | 8.38    | 7.14  | 117.4 |
| Average      | 33.13   | 20.01 | 59.30    | 35.81 | 16.32     | 9.85  | 45.27    | 27.34 | 11.57   | 6.99  | 165.6 |
| St.deviation | 3.72    | 2.25  | 30.81    | 18.61 | 2.55      | 1.54  | 23.10    | 13.95 | 2.87    | 1.73  | 63.0  |
| Fe           | Phase I |       | Phase II |       | Phase III |       | Phase IV |       | Phase V |       | Total |
|              | ppm     | %     | ppm      | %     | ppm       | %     | ppm      | %     | ppm     | %     | ppm   |
| Sample1      | 6.30    | 0.20  | 0.17     | 0.01  | 1741      | 55.49 | 983.3    | 31.34 | 406.9   | 12.97 | 3138  |
| Sample2      | 8.96    | 0.27  | 0.16     | 0.00  | 1755      | 53.30 | 1002.0   | 30.43 | 526.3   | 15.99 | 3292  |
| Sample3      | 4.96    | 0.18  | 0.00     | 0.00  | 1767      | 65.25 | 505.7    | 18.68 | 430.2   | 15.89 | 2708  |
| Sample4      | 15.03   | 0.61  | 0.00     | 0.00  | 1780      | 72.52 | 495.0    | 20.17 | 164.3   | 6.69  | 2454  |
| Average      | 8.81    | 0.30  | 0.08     | 0.00  | 1761      | 60.76 | 746.5    | 25.76 | 382.0   | 13.18 | 2898  |
| St.deviation | 4.47    | 0.15  | 0.10     | 0.00  | 17        | 0.57  | 284.4    | 9.81  | 154.0   | 5.31  | 460   |

TABLE II. Concentrations of extracted chromium, manganese, nickel, copper and zinc (ppm) from milled lignite samples used in the "Nikola Tesla" power plants

| Cr           | Phase I |      | Phase II |      | Phase III |       | Phase IV |       | Phase V |       | Total |   |
|--------------|---------|------|----------|------|-----------|-------|----------|-------|---------|-------|-------|---|
|              | ppm     | %    | ppm      | %    | ppm       | %     | ppm      | %     | ppm     | %     | ppm   | % |
| Sample1      | 0.01    | 0.12 | 0.00     | 0.00 | 0.90      | 10.38 | 5.76     | 66.44 | 2.00    | 23.07 | 8.67  |   |
| Sample2      | 0.02    | 0.14 | 1.39     | 9.82 | 1.00      | 7.07  | 8.33     | 58.87 | 3.41    | 24.10 | 14.15 |   |
| Sample3      | 0.26    | 1.90 | 0.04     | 0.29 | 1.05      | 7.66  | 9.35     | 68.25 | 3.00    | 21.90 | 13.70 |   |
| Sample4      | 0.13    | 1.42 | 0.03     | 0.33 | 1.10      | 12.00 | 7.91     | 86.26 | 0.00    | 0.00  | 9.17  |   |
| Average      | 0.11    | 0.92 | 0.37     | 3.20 | 1.01      | 8.86  | 7.84     | 68.61 | 2.10    | 18.41 | 11.42 |   |
| St.deviation | 0.12    | 1.02 | 0.68     | 5.98 | 0.09      | 0.75  | 1.51     | 13.23 | 1.52    | 13.32 | 3.92  |   |
| Mn           | Phase I |      | Phase II |      | Phase III |       | Phase IV |       | Phase V |       | Total |   |
|              | ppm     | %    | ppm      | %    | ppm       | %     | ppm      | %     | ppm     | %     | ppm   | % |
| Sample1      | 1.96    | 0.82 | 14.47    | 6.08 | 101.40    | 42.60 | 24.35    | 10.23 | 95.83   | 40.26 | 238.0 |   |
| Sample2      | 1.49    | 0.67 | 13.62    | 6.10 | 84.20     | 37.72 | 20.14    | 9.02  | 103.8   | 46.49 | 223.2 |   |
| Sample3      | 1.58    | 1.08 | 8.26     | 5.64 | 49.19     | 33.57 | 8.04     | 5.49  | 79.44   | 54.22 | 146.5 |   |
| Sample4      | 1.13    | 1.03 | 8.13     | 7.38 | 53.20     | 48.29 | 6.95     | 6.31  | 40.76   | 37.00 | 110.2 |   |
| Average      | 1.54    | 0.86 | 11.12    | 6.20 | 72.00     | 40.11 | 14.87    | 8.28  | 80.0    | 44.55 | 179.5 |   |
| St.deviation | 0.34    | 0.19 | 3.40     | 1.89 | 25.08     | 13.97 | 8.70     | 4.85  | 28.0    | 15.62 | 65.6  |   |
| Ni           | Phase I |      | Phase II |      | Phase III |       | Phase IV |       | Phase V |       | Total |   |
|              | ppm     | %    | ppm      | %    | ppm       | %     | ppm      | %     | ppm     | %     | ppm   | % |
| Sample1      | 0.13    | 0.46 | 0.07     | 0.25 | 16.68     | 58.49 | 9.18     | 32.19 | 2.46    | 8.63  | 28.52 |   |
| Sample2      | 0.15    | 0.45 | 0.08     | 0.24 | 16.28     | 48.60 | 12.05    | 35.97 | 4.94    | 14.75 | 33.50 |   |
| Sample3      | 0.10    | 0.40 | 0.05     | 0.20 | 14.47     | 57.33 | 6.72     | 26.62 | 3.90    | 15.45 | 25.24 |   |
| Sample4      | 0.16    | 0.71 | 0.05     | 0.22 | 14.85     | 66.35 | 5.82     | 26.01 | 1.50    | 6.70  | 22.38 |   |
| Average      | 0.14    | 0.49 | 0.06     | 0.23 | 15.57     | 56.80 | 8.44     | 30.80 | 3.20    | 11.67 | 27.41 |   |

TABLE II. Continued

| St.deviation | 0.03    | 0.10  | 0.02     | 0.05  | 1.07      | 3.92  | 2.79     | 10.19 | 1.52    | 5.56  | 5.43  |
|--------------|---------|-------|----------|-------|-----------|-------|----------|-------|---------|-------|-------|
| Cu           | Phase I | %     | Phase II | %     | Phase III | %     | Phase IV | %     | Phase V | %     | Total |
|              | ppm     |       | ppm      |       | ppm       |       | ppm      |       | ppm     |       | ppm   |
| Sample1      | 0.06    | 0.43  | 0.02     | 0.14  | 9.21      | 65.37 | 1.80     | 12.78 | 3.00    | 21.29 | 14.09 |
| Sample2      | 0.07    | 0.45  | 0.03     | 0.19  | 9.45      | 60.69 | 1.68     | 10.79 | 4.34    | 27.87 | 15.57 |
| Sample3      | 0.08    | 0.63  | 0.02     | 0.16  | 8.31      | 65.28 | 1.02     | 8.01  | 3.30    | 25.92 | 12.73 |
| Sample4      | 0.09    | 0.94  | 0.01     | 0.10  | 7.31      | 76.38 | 1.26     | 13.17 | 0.90    | 9.40  | 9.57  |
| Average      | 0.08    | 0.58  | 0.02     | 0.15  | 8.57      | 65.97 | 1.44     | 11.09 | 2.89    | 22.21 | 12.99 |
| St.deviation | 0.01    | 0.10  | 0.01     | 0.06  | 0.97      | 7.49  | 0.36     | 2.80  | 1.44    | 11.10 | 2.80  |
| Zn           | Phase I | %     | Phase II | %     | Phase III | %     | Phase IV | %     | Phase V | %     | Total |
|              | ppm     |       | ppm      |       | ppm       |       | ppm      |       | ppm     |       | ppm   |
| Sample1      | 0.23    | 1.02  | 0.29     | 1.29  | 9.52      | 42.20 | 3.02     | 13.39 | 9.50    | 42.11 | 22.56 |
| Sample2      | 3.60    | 8.70  | 5.77     | 13.94 | 13.03     | 31.47 | 4.05     | 9.78  | 14.95   | 36.11 | 41.40 |
| Sample3      | 6.48    | 18.77 | 0.25     | 0.72  | 13.78     | 39.92 | 1.72     | 4.98  | 12.29   | 35.60 | 34.52 |
| Sample4      | 4.89    | 16.79 | 0.49     | 1.68  | 16.64     | 57.12 | 3.11     | 10.68 | 4.00    | 13.73 | 29.13 |
| Average      | 3.80    | 11.91 | 1.70     | 5.33  | 13.24     | 41.51 | 2.98     | 9.33  | 10.19   | 31.93 | 31.90 |
| St.deviation | 2.66    | 8.32  | 2.72     | 8.51  | 2.93      | 9.18  | 0.96     | 3.00  | 4.69    | 14.69 | 13.94 |

TABLE III. Concentrations of extracted arsenic, cadmium and lead (ppm) from milled lignite samples used in the "Nikola Tesla" power plants

| As           | Phase I |       | Phase II |      | Phase III |       | Phase IV |       | Phase V |       | Total |
|--------------|---------|-------|----------|------|-----------|-------|----------|-------|---------|-------|-------|
|              | ppm     | %     | ppm      | %    | ppm       | %     | ppm      | %     | ppm     | %     |       |
| Sample1      | 2.09    | 19.28 | 0.00     | 0.00 | 1.42      | 13.10 | 5.76     | 53.14 | 1.57    | 14.48 | 10.84 |
| Sample2      | 2.21    | 17.88 | 0.00     | 0.00 | 0.37      | 2.99  | 6.93     | 56.07 | 2.85    | 23.06 | 12.36 |
| Sample3      | 0.28    | 2.92  | 0.01     | 0.10 | 1.38      | 14.39 | 5.42     | 56.52 | 2.50    | 26.07 | 9.59  |
| Sample4      | 1.74    | 39.37 | 0.00     | 0.00 | 0.37      | 8.37  | 2.30     | 52.04 | 0.01    | 0.23  | 4.42  |
| Average      | 1.58    | 16.98 | 0.00     | 0.03 | 0.89      | 9.51  | 5.10     | 54.85 | 1.73    | 18.62 | 9.30  |
| St.deviation | 0.89    | 9.56  | 0.01     | 0.05 | 0.59      | 6.40  | 1.98     | 21.25 | 1.27    | 13.64 | 4.74  |
| Cd           | Phase I |       | Phase II |      | Phase III |       | Phase IV |       | Phase V |       | Total |
|              | ppm     | %     | ppm      | %    | Ppm       | %     | ppm      | %     | ppm     | %     |       |
| Sample1      | 0.00    | 0.00  | 0.00     | 0.00 | 0.00      | 0.00  | 0.00     | 0.00  | 0.15    | 100.0 | 0.15  |
| Sample2      | 0.00    | 0.00  | 0.01     | 6.25 | 0.00      | 0.00  | 0.00     | 0.00  | 0.15    | 93.75 | 0.16  |
| Sample3      | 0.00    | 0.00  | 0.01     | 6.25 | 0.00      | 0.00  | 0.00     | 0.00  | 0.15    | 93.75 | 0.16  |
| Sample4      | 0.00    | 0.00  | 0.01     | 6.25 | 0.00      | 0.00  | 0.00     | 0.00  | 0.15    | 93.75 | 0.16  |
| Average      | 0.00    | 0.00  | 0.01     | 4.76 | 0.00      | 0.00  | 0.00     | 0.00  | 0.15    | 95.24 | 0.16  |
| St.deviation | 0.00    | 0.00  | 0.01     | 3.17 | 0.00      | 0.00  | 0.00     | 0.00  | 0.00    | 0.00  | 0.01  |
| Pb           | Phase I |       | Phase II |      | Phase III |       | Phase IV |       | Phase V |       | Total |
|              | ppm     | %     | ppm      | %    | Ppm       | %     | ppm      | %     | ppm     | %     |       |
| Sample1      | 0.00    | 0.00  | 0.00     | 0.00 | 0.00      | 0.00  | 0.66     | 9.95  | 5.97    | 90.05 | 6.63  |
| Sample2      | 0.00    | 0.00  | 0.00     | 0.00 | 0.40      | 3.48  | 0.60     | 5.22  | 10.49   | 91.30 | 11.49 |
| Sample3      | 0.00    | 0.00  | 0.00     | 0.00 | 0.00      | 0.00  | 1.14     | 11.09 | 9.14    | 88.91 | 10.28 |
| Sample4      | 0.00    | 0.00  | 0.00     | 0.00 | 0.00      | 0.00  | 0.90     | 26.47 | 2.50    | 73.53 | 3.40  |
| Average      | 0.00    | 0.00  | 0.00     | 0.00 | 0.10      | 1.26  | 0.83     | 10.38 | 7.03    | 88.36 | 7.95  |
| St.deviation | 0.00    | 0.00  | 0.00     | 0.00 | 0.20      | 2.52  | 0.25     | 3.10  | 3.56    | 44.81 | 4.01  |



TABLE IV. Correlational parameters (correlational coefficient  $R$  and significance of correlation  $p$ ) of the concentrations extracted in the fifth phase of the sequential extraction of samples of milled lignite. Correlations with a significance of correlation  $p \leq 0.05$  are shaded

|    |   | Mg    | Al    | Si    | K     | Fe    | Cr    | Mn    | Ni    | Cu    | Zn    | As    | Cd    | Pb    |
|----|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Mg | R |       | 0.990 | 0.962 | 0.870 | 0.997 | 0.984 | 0.930 | 0.936 | 0.999 | 0.991 | 0.981 | -0.31 | 0.968 |
|    | p |       | 0.010 | 0.038 | 0.130 | 0.016 | 0.016 | 0.070 | 0.064 | 0.001 | 0.009 | 0.019 | 0.694 | 0.032 |
| Al | R | 0.990 |       | 0.964 | 0.869 | 0.994 | 0.990 | 0.930 | 0.901 | 0.988 | 0.978 | 0.984 | -0.18 | 0.958 |
|    | p | 0.010 |       | 0.036 | 0.131 | 0.006 | 0.010 | 0.070 | 0.099 | 0.012 | 0.022 | 0.016 | 0.821 | 0.042 |
| Si | R | 0.962 | 0.964 |       | 0.969 | 0.946 | 0.992 | 0.806 | 0.962 | 0.951 | 0.985 | 0.996 | -0.30 | 0.996 |
|    | p | 0.038 | 0.036 |       | 0.031 | 0.054 | 0.008 | 0.194 | 0.038 | 0.049 | 0.015 | 0.004 | 0.701 | 0.004 |
| K  | R | 0.870 | 0.869 | 0.969 |       | 0.838 | 0.930 | 0.634 | 0.950 | 0.852 | 0.924 | 0.943 | -0.37 | 0.965 |
|    | p | 0.130 | 0.131 | 0.031 |       | 0.162 | 0.070 | 0.366 | 0.050 | 0.148 | 0.076 | 0.057 | 0.631 | 0.035 |
| Fe | R | 0.997 | 0.994 | 0.946 | 0.838 |       | 0.977 | 0.953 | 0.905 | 0.998 | 0.978 | 0.971 | -0.24 | 0.948 |
|    | p | 0.016 | 0.006 | 0.054 | 0.162 |       | 0.023 | 0.047 | 0.095 | 0.002 | 0.022 | 0.029 | 0.759 | 0.052 |

TABLE V. Correlational parameters (correlational coefficient  $R$  and significance of correlation  $p$ ) of the concentrations extracted in the third phase of the sequential extraction of samples of milled lignite. Correlations with a significance of correlation  $p \leq 0.05$  are shaded

|    |   | Mg    | Al    | Si    | K     | Fe    | Cr    | Mn    | Ni    | Cu    | Zn    | As    | Cd  | Pb    |
|----|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-----|-------|
| Mg | R |       | 0.981 | 0.984 | 0.947 | -0.89 | -0.82 | 0.850 | 0.856 | 0.995 | -0.81 | 0.167 | --- | 0.629 |
|    | p |       | 0.019 | 0.016 | 0.053 | 0.105 | 0.182 | 0.150 | 0.143 | 0.005 | 0.193 | 0.833 | --- | 0.371 |
| Al | R | 0.981 |       | 1.000 | 0.978 | -0.80 | -0.70 | 0.737 | 0.759 | 0.984 | -0.70 | 0.090 | --- | 0.732 |
|    | p | 0.019 |       | 0.000 | 0.022 | 0.198 | 0.299 | 0.263 | 0.241 | 0.016 | 0.298 | 0.909 | --- | 0.268 |
| Si | R | 0.984 | 1.000 |       | 0.980 | -0.82 | -0.72 | 0.746 | 0.764 | 0.988 | -0.72 | 0.112 | --- | 0.716 |
|    | p | 0.016 | 0.000 |       | 0.020 | 0.184 | 0.284 | 0.254 | 0.236 | 0.012 | 0.282 | 0.888 | --- | 0.285 |
| K  | R | 0.947 | 0.978 | 0.980 |       | -0.79 | -0.69 | 0.644 | 0.644 | 0.970 | -0.72 | 0.242 | --- | 0.647 |
|    | p | 0.053 | 0.022 | 0.020 |       | 0.209 | 0.313 | 0.356 | 0.355 | 0.030 | 0.282 | 0.758 | --- | 0.353 |
| Fe | R | -0.89 | -0.80 | -0.82 | -0.79 |       | 0.988 | -0.92 | -0.86 | -0.89 | 0.982 | -0.50 | --- | -0.22 |
|    | p | 0.105 | 0.198 | 0.184 | 0.209 |       | 0.012 | 0.083 | 0.135 | 0.106 | 0.018 | 0.504 | --- | 0.778 |

TABLE VI. Correlational parameters (correlational coefficient  $R$  and significance of correlation  $p$ ) of the concentrations of the major elements extracted in the fifth and third phase of the sequential extraction with the concentrations of major and trace elements extracted in the first phase of the sequential extraction of samples of milled lignite. Correlations with a significance of correlation  $p \leq 0.05$  are shaded

|    |   | Mg    | Al    | Si    | K     | Fe    | Cr    | Mn    | Ni    | Cu    | Zn    | As    | Cd | Pb |
|----|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|----|----|
| Mg | R | 0.503 | -0.80 | -0.72 | -0.75 | -0.73 | -0.20 | 0.532 | -0.35 | -0.61 | -0.11 | -0.00 | —  | —  |
|    | p | 0.497 | 0.197 | 0.280 | 0.250 | 0.268 | 0.798 | 0.468 | 0.649 | 0.393 | 0.881 | 0.997 | —  | —  |
| Al | R | 0.571 | -0.85 | -0.80 | -0.80 | -0.82 | -0.13 | 0.610 | -0.47 | -0.64 | -0.12 | -0.09 | —  | —  |
|    | p | 0.429 | 0.153 | 0.202 | 0.200 | 0.181 | 0.865 | 0.390 | 0.531 | 0.363 | 0.877 | 0.910 | —  | —  |
| Si | R | 0.707 | -0.68 | -0.66 | -0.62 | -0.75 | 0.069 | 0.408 | -0.49 | -0.41 | 0.140 | -0.26 | —  | —  |
|    | p | 0.293 | 0.315 | 0.339 | 0.377 | 0.249 | 0.931 | 0.592 | 0.505 | 0.590 | 0.860 | 0.744 | —  | —  |
| K  | R | 0.802 | -0.49 | -0.50 | -0.42 | -0.65 | 0.271 | 0.203 | -0.51 | -0.17 | 0.381 | -0.41 | —  | —  |
|    | p | 0.198 | 0.507 | 0.499 | 0.578 | 0.347 | 0.729 | 0.797 | 0.492 | 0.827 | 0.619 | 0.587 | —  | —  |
| Fe | R | 0.484 | -0.85 | -0.77 | -0.80 | -0.77 | -0.23 | 0.598 | -0.37 | -0.66 | -0.18 | 0.015 | —  | —  |
|    | p | 0.517 | 0.152 | 0.231 | 0.199 | 0.234 | 0.767 | 0.402 | 0.627 | 0.334 | 0.816 | 0.985 | —  | —  |
| Mg | R | -0.01 | -0.88 | -0.71 | -0.86 | -0.56 | -0.68 | 0.703 | -0.03 | -0.88 | -0.64 | 0.484 | —  | —  |
|    | p | 0.990 | 0.122 | 0.290 | 0.139 | 0.439 | 0.315 | 0.297 | 0.973 | 0.112 | 0.363 | 0.516 | —  | —  |
| Al | R | 0.106 | -0.84 | -0.67 | -0.81 | -0.56 | -0.59 | 0.604 | -0.46 | -0.79 | -0.48 | 0.400 | —  | —  |
|    | p | 0.894 | 0.162 | 0.330 | 0.195 | 0.437 | 0.409 | 0.396 | 0.954 | 0.208 | 0.520 | 0.600 | —  | —  |
| Si | R | 0.108 | -0.85 | -0.68 | -0.82 | -0.58 | -0.59 | 0.623 | -0.60 | -0.81 | -0.49 | 0.396 | —  | —  |
|    | p | 0.892 | 0.150 | 0.315 | 0.181 | 0.423 | 0.409 | 0.377 | 0.940 | 0.194 | 0.508 | 0.604 | —  | —  |
| K  | R | 0.301 | -0.89 | -0.77 | -0.86 | -0.71 | -0.42 | 0.663 | -0.25 | -0.78 | -0.38 | 0.205 | —  | —  |
|    | p | 0.699 | 0.109 | 0.227 | 0.145 | 0.289 | 0.576 | 0.337 | 0.753 | 0.219 | 0.624 | 0.795 | —  | —  |
| Fe | R | 0.066 | 0.934 | 0.840 | 0.952 | 0.655 | 0.644 | -0.92 | 0.202 | 0.999 | 0.820 | -0.41 | —  | —  |
|    | p | 0.934 | 0.065 | 0.160 | 0.048 | 0.345 | 0.356 | 0.077 | 0.798 | 0.000 | 0.180 | 0.591 | —  | —  |

TABLE VII. Correlational parameters (correlational coefficient  $R$  and significance of correlation  $p$ ) of the concentrations of the major elements extracted in the fifth and third phase of the sequential extraction with the concentrations of major and trace elements extracted in the second phase of the sequential extraction of samples of milled lignite. Correlations with a significance of correlation  $p \leq 0.05$  are shaded

|    |   | Mg    | Al    | Si    | K     | Fe    | Cr    | Mn    | Ni    | Cu    | Zn    | As    | Cd    | Pb |
|----|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|----|
| Mg | R | 0.551 | 0.224 | 0.876 | 0.402 | 0.588 | 0.662 | 0.567 | 0.690 | 0.964 | 0.635 | 0.243 | -0.02 | —  |
|    | p | 0.449 | 0.776 | 0.124 | 0.599 | 0.412 | 0.338 | 0.433 | 0.310 | 0.036 | 0.365 | 0.757 | 0.985 | —  |
| Al | R | 0.431 | 0.311 | 0.815 | 0.461 | 0.552 | 0.552 | 0.540 | 0.620 | 0.920 | 0.523 | 0.348 | -0.08 | —  |
|    | p | 0.569 | 0.689 | 0.186 | 0.539 | 0.448 | 0.448 | 0.460 | 0.380 | 0.080 | 0.477 | 0.652 | 0.919 | —  |
| Si | R | 0.449 | 0.459 | 0.735 | 0.630 | 0.345 | 0.581 | 0.322 | 0.479 | 0.883 | 0.548 | 0.447 | 0.173 | —  |
|    | p | 0.551 | 0.541 | 0.265 | 0.370 | 0.655 | 0.419 | 0.678 | 0.521 | 0.117 | 0.452 | 0.553 | 0.827 | —  |
| K  | R | 0.414 | 0.586 | 0.600 | 0.761 | 0.118 | 0.550 | 0.088 | 0.300 | 0.781 | 0.514 | 0.530 | 0.392 | —  |
|    | p | 0.586 | 0.414 | 0.400 | 0.239 | 0.882 | 0.450 | 0.912 | 0.700 | 0.219 | 0.486 | 0.470 | 0.608 | —  |
| Fe | R | 0.511 | 0.209 | 0.872 | 0.372 | 0.625 | 0.621 | 0.610 | 0.701 | 0.954 | 0.595 | 0.244 | -0.10 | —  |
|    | p | 0.489 | 0.791 | 0.127 | 0.628 | 0.375 | 0.379 | 0.391 | 0.299 | 0.046 | 0.405 | 0.746 | 0.905 | —  |
| Mg | R | 0.568 | -0.28 | 0.926 | -0.14 | 0.936 | 0.614 | 0.929 | 0.928 | 0.876 | 0.607 | -0.19 | -0.44 | —  |
|    | p | 0.432 | 0.722 | 0.074 | 0.855 | 0.064 | 0.387 | 0.071 | 0.072 | 0.123 | 0.393 | 0.811 | 0.559 | —  |
| Al | R | 0.661 | -0.18 | 0.972 | -0.02 | 0.868 | 0.721 | 0.849 | 0.919 | 0.953 | 0.710 | -0.13 | -0.26 | —  |
|    | p | 0.339 | 0.815 | 0.028 | 0.984 | 0.132 | 0.279 | 0.151 | 0.081 | 0.047 | 0.290 | 0.869 | 0.736 | —  |
| Si | R | 0.643 | -0.18 | 0.967 | -0.02 | 0.872 | 0.704 | 0.855 | 0.916 | 0.948 | 0.693 | -0.12 | -0.28 | —  |
|    | p | 0.357 | 0.820 | 0.033 | 0.984 | 0.128 | 0.296 | 0.145 | 0.084 | 0.052 | 0.307 | 0.878 | 0.715 | —  |
| K  | R | 0.550 | 0.019 | 0.924 | 0.176 | 0.774 | 0.638 | 0.761 | 0.817 | 0.956 | 0.619 | 0.078 | -0.24 | —  |
|    | p | 0.450 | 0.981 | 0.076 | 0.824 | 0.226 | 0.362 | 0.239 | 0.183 | 0.044 | 0.381 | 0.922 | 0.759 | —  |
| Fe | R | -0.16 | 0.239 | -0.66 | 0.222 | -0.89 | -0.20 | -0.91 | -0.73 | -0.60 | -0.20 | 0.073 | 0.782 | —  |
|    | p | 0.836 | 0.761 | 0.339 | 0.778 | 0.112 | 0.798 | 0.086 | 0.268 | 0.399 | 0.803 | 0.927 | 0.218 | —  |

The investigated major elements (Table I) can be separated on the basis of their fraction in the extracted organic/sulfide phase into elements which were predominantly extracted from this phase (aluminium  $58.56 \pm 11.31$  % and silicon  $58.36 \pm 11.66$  %) and into those which were predominantly extracted from the inorganic component, even in an extracted fraction of lignite (iron 60.76 % of the totally extracted elements was released in the third phase of the extraction). It is interesting to note that two major elements, magnesium and potassium, cannot be precisely categorized. Actually, a larger amount of potassium and approximately the same amount of magnesium were released in the fourth phase of the sequential extraction compared with the sum of the amounts extracted in the third and the fifth phase, however, more than 50 % of the extracted amounts were released in the first two phases of the sequential extraction. Since it is not possible to determine the origin of adsorbed and ion-exchangeable fraction using the applied technique (only the correlation of adsorbed potassium with iron released in the third phase is significant), it is not possible to say whether the adsorbed and ion-exchangeable potassium and magnesium were connected with the organic or with the inorganic fraction of lignite.

Concerning the microelements (Tables II and III), they can be classified into three groups. Elements having a large part of their extractable component associated with the extracted organic/sulfide fraction of lignite are in the first group, *i.e.*, chromium ( $68.61 \pm 13.23$  %) and arsenic ( $54.85 \pm 21.25$  %). Elements having a significant (although less than 50 %) amount of their extractable component connected with the extracted organic/sulfide phase are in the second group, the main representative being nickel ( $30.80 \pm 10.19$  %). The extracted organic/sulfide component of the other investigated elements, which are in the third group, are present in only small amounts, *i.e.*, manganese ( $8.28 \pm 4.85$  %), copper ( $11.09 \pm 2.80$  %), zinc ( $9.33 \pm 3.00$  %), cadmium ( $0.00 \pm 0.00$  %) and lead ( $10.38 \pm 3.10$  %) of the total extracted amount.

The fact that most of the elements are indisputably connected with the inorganic fraction of lignite is not unexpected taking into consideration the large amount of ash remaining after the combustion of lignite. The elements within the extractable fraction, which are prevalently connected with the inorganic component can be divided into subgroups based on the difference of their extractability in the third and fifth phase of the sequential extraction of the lignite. The first group contains elements the extractable fraction of which is connected with the inorganic component and is concentrated in the third phase of the sequential extraction. The second group contains elements the extractable fractions of which, except for the part which is organically associated, are mostly present in the fifth phase of the sequential extraction. Nickel ( $56.80 \pm 3.92$  % extracted in the third and  $11.67 \pm 5.56$  % extracted in the fifth phase of the sequential extraction), copper ( $65.97 \pm 7.49$  % extracted in the third and  $22.21 \pm 11.10$  % extracted in the fifth phase of the sequen-

tial extraction) and iron ( $60.76 \pm 0.57$  % extracted in the third and  $13.18 \pm 5.31$  % extracted in the fifth phase of the sequential extraction) belong to the first group. Cadmium ( $0.00 \pm 0.00$  % extracted in the third and  $95.24 \pm 0.00$  % extracted in the fifth phase of the sequential extraction) and lead ( $1.26 \pm 2.52$  % extracted in the third and  $88.36 \pm 44.81$  % extracted in the fifth phase of the sequential extraction) belong to the second group, while zinc ( $41.51 \pm 9.18$  % extracted in the third and  $31.93 \pm 14.69$  % extracted in the fifth phase of the sequential extraction) and manganese ( $40.11 \pm 13.97$  % extracted in the third and  $44.55 \pm 15.62$  % extracted in the fifth phase of the sequential extraction) lie between these two groups.

It is possible to make an assumption about the association of the elements present in inorganic fraction of lignite on the basis of intraphase correlation analysis of the concentrations which are extracted in phases of the sequential extraction where inorganic matrix was dissolved, *i.e.*, third and fifth phase. Correlational parameters (correlational coefficient  $R$  and significance of correlation  $p$ ) of the concentrations extracted in the fifth and third phase of sequential extraction of samples of milled lignite are shown in Tables IV and V, respectively.

There is a strong correlation (*i.e.*, correlation having a significance of correlation  $p \leq 0.05$ ) between the concentrations of magnesium, aluminum, and silicon leached in the fifth phase of sequential extraction (Table IV), suggesting that magnesium aluminosilicates (and/or magnesium aluminates, magnesium silicates and aluminosilicates which do not contain magnesium) are dissolved in this phase of the extraction. Of the other examined major elements, the concentrations of potassium dissolved in the fifth phase are significantly correlated with concentrations of silicon dissolved in the same phase, while the concentrations of iron are significantly correlated with the concentrations of magnesium and aluminum leached in the fifth phase of the sequential extraction. This is probably a result of the dissolution of silicates of potassium and mixed aluminates of iron and magnesium (and/or magnesium aluminates, iron aluminates, and compounds of iron and magnesium which do not contain aluminum) in this phase of the sequential extraction. On the base of the results obtained by statistical analysis of the concentrations of trace and major elements dissolved in the fifth phase of the extraction (Table IV), it is possible to conclude that mixed aluminates of iron and magnesium (and/or magnesium aluminates and compounds of iron and magnesium which do not contain aluminum) are the carriers of arsenic, zinc, copper and chromium, while magnesium aluminosilicates (and/or magnesium aluminates, magnesium silicates and aluminosilicates which do not contain magnesium) are, in addition, also scavengers of lead. Potassium silicates extracted in the last phase of sequential extraction are the scavengers of lead and nickel. Finally, manganese is substrate of iron compounds not associated with the aluminum leached in the last phase of the extraction.

Statistical analysis of the concentrations of elements leached in the third phase of sequential extraction (Table V), the second phase in which inorganic matrix par-

ticles are dissolved, revealed fewer correlations of high significance than the analysis of the concentrations obtained in the fifth phase of the extraction. Alumosilicates are again present as carriers which are dissolved in this phase of the extraction, as can be seen by the significant correlation of the concentrations of leached aluminum and silicon. The concentrations of both elements are significantly correlated with the concentration of extracted potassium and magnesium, thus evidencing the existence of alumosilicates of potassium (and/or potassium aluminates, potassium silicates and alumosilicates which do not contain potassium) and magnesium alumosilicates (and/or magnesium aluminates, magnesium silicates and alumosilicates which do not contain magnesium) which are leached in this phase of the extraction. Based on statistical analysis, it can be said that copper is a substrate of these compounds, while zinc and chromium are substrates of iron compounds extracted in the third phase. The intraphase correlational analysis (although based on the measured concentrations of some elements only) revealed the existence of at least four different inorganic scavengers of copper, at least three different inorganic carriers of chromium and zinc, two of lead and arsenic and one of manganese and nickel.

The interphase correlation (the results are shown in Tables VI and VII), *i.e.*, the correlation between the concentrations extracted in different phases, was performed here mainly to establish certain regularities in the binding of the easily mobile fractions, the first and the second ones, on the one hand, and the parts of the component of the inorganic matrix, on the other. Thus, on the basis of the interphase correlations, it was possible to postulate that the ion-exchangeable silicon is most probably bound to alumosilicates which do not contain potassium and which are dissolved in the third phase of the extraction, while the ion-exchangeable copper is bound to potassium aluminates dissolved in the third phase, and compounds of magnesium and iron dissolved in the fifth phase of the extraction. The adsorbed fraction of copper is preferably bound to iron compounds dissolved in the third phase of the extraction.

However, it can be noticed that the concentrations of most of the adsorbed and ion-exchangeable fractions of the analyzed trace and major elements do not reveal significant correlations with the concentrations of the major elements soluble in the third and the fifth phase of the sequential extraction. There are several possible explanations for this. The most elegant one is that almost all the elements are adsorbed or bound by ion-exchangeable bonds with the organic and/or sulfide component of lignite (or with compounds of the macro elements which were not investigated, calcium foremostly), and, hence, their concentrations cannot be significantly correlated with the concentrations of the major elements of the inorganic matrix of lignite. Although this fact is probably partially correct, it is not possible to explain all the potential associations between the elements by employing it. There are a large number of significant interphase correlations on a not significantly changed inorganic matrix in both the fly ash and landfill ash,<sup>26</sup> which

proves the possibility or sensibility of the inorganic matrix for this kind of bonding. The relatively small number of significant correlations of this kind in the lignite samples can still be a consequence of non-selective bonding of adsorbed and ion-exchangeable fractions of different elements, due to which the significance of the correlations is lost.

The question arises as to the origin of the adsorbed and ion-exchangeable fraction in the investigated samples of lignite. These two fractions of different elements certainly existed in the original samples of lignites but it is questionable whether the adsorbed and ion-exchangeable elements, which were present in the original lignite, were also present in the lignite used in the thermo-electric power plant, or whether these fractions present during the combustion of the lignite were of a more recent origin. Taking into consideration that the lignite had been exposed to rain after its mining, *i.e.*, in stock piles and during transportation, it is probable that most of the elements which were present in the original “easily extractable” fractions of lignite were rinsed out long before the combustion process, and that the experimentally found adsorbed and ion-exchangeable elements, were present as a consequence of sorption occurring during transportation, storage and grinding of the lignite.

#### CONCLUSIONS

- The largest fractions of the examined elements were associated with the extractable inorganic fractions of lignite, only aluminum, silicon, chromium and arsenic had larger extractable organic/sulfide than extractable inorganic fractions.
- Within the inorganic fraction, larger amounts of nickel, copper, iron, zinc and manganese were extracted in the third than in the fifth phase, while the opposite was true in the cases of cadmium and lead.
- Aluminosilicates of magnesium (and/or aluminates of magnesium, silicates of magnesium and aluminosilicates that do not contain magnesium) which were carriers of arsenic, zinc, lead, copper and chromium, silicates of potassium which were carriers of lead and nickel, mixed aluminates of iron and magnesium (and/or aluminates of iron, aluminates of magnesium and compounds containing iron and magnesium but not aluminum) which were carriers of arsenic, zinc, copper and chromium, and compounds of iron that do not contain aluminum and magnesium which were scavengers of manganese were dissolved in the fifth phase of the sequential extraction.
- Copper is a substrate of aluminosilicates of potassium (and/or aluminates of potassium, silicates of potassium and aluminosilicates containing no potassium) and aluminosilicates of magnesium (and/or aluminates of magnesium, silicates of magnesium and aluminosilicates which do not contain magnesium) dissolved in the third phase of the extraction, while compounds of iron leached in the same phase were carriers of zinc and chromium.
- Copper is adsorbed to iron dissolved in the third phase of the sequential extraction, while the ion-exchangeable fraction of the same element was bound to



compounds of the manganese and iron dissolved in the fifth, and aluminum and potassium extracted in the third phase of the sequential extraction. Ion-exchangeable silicon is bound to aluminosilicates washed in the third phase of the extraction.

– Most of the adsorbed and ion-exchangeable elements do not specifically bind to the parts of the inorganic fractions of the matrix

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#### ИЗВОД

#### СПЕЦИЈАЦИЈА ОДАБРАНИХ МИКРО- И МАКРОЕЛЕМЕНАТА У УЗОРЦИМА ЛИГНИТА ТЕРМОЕЛЕКТРАНЕ "НИКОЛА ТЕСЛА А" (ОБРЕНОВАЦ, СРБИЈА)

АЛЕКСАНДАР ПОПОВИЋ<sup>1</sup> и ДРАГАНА ЂОРЂЕВИЋ<sup>2</sup>

<sup>1</sup>Хемијски факултет, Универзитет у Београду, б. бр. 158, 11001 Београд и <sup>2</sup>ИХТМ- Центар за хемију, Ђеђошева 12, 11000 Београд

Четири узорка млевеног лигнита коришћеног у Термоелектрани "Никола Тесла А" у Обреновцу у Београда су подвргнута секвенцијалној екстракцији која се састојала од пет фаза: у првој је коришћена дестилована вода, у другој 1 М амонијум-ацетат, у трећој 0,2 М амонијум-оксалат и 0,2 М оксална киселина, у четвртој кисео раствор  $H_2O_2$  и у петој 6 М раствор  $HCl$ . Добијене концентрације изабраних елемената су статистички анализирани, како би се утврдиле везе између различитих елемената. Највећи део испитиваних елемената је углавном асоциран са екстрахованом неорганском фазом угља, само алуминијум, силицијум, хром и арсен имају унутар екстрактивбилног дела елемената већу органску/сулфидну фракцију од неорганске. Од једињења растворних у петој фази екстракције угља, алумосиликати магнезијума су носилац арсена, цинка, олова, бакра и хрома, силикати калијума носилац олова и никла, мешовити алуминати гвожђа и магнезијума носилац арсена, цинка, бакра и хрома, а једињења гвожђа која нису повезана са алуминатима ни магнезијумом носилац мангана. У трећој фази екстракције угља се растварају алумосиликати калијума и магнезијума асоцирани са баком, док су једињења гвожђа растворна у трећој фази екстракције асоцирана са цинком и хромом. Интерфазна корелациона анализа је показала да се адсорбована и јоноизмењива фракција већине испитиваних елемената не везује преференцијално за делове неорганске матрице честица пепела.

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